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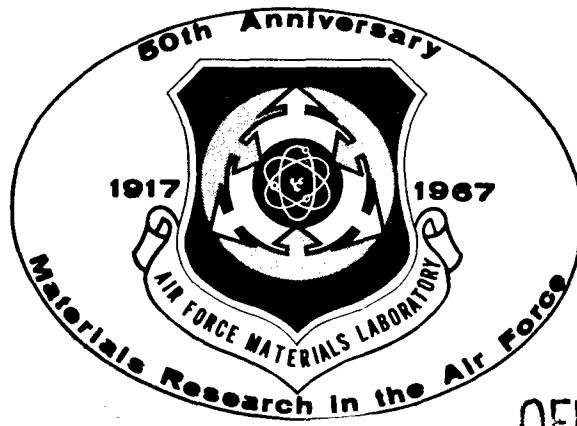
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TECHNICAL REPORT AFML-TR-67-431

MAY 1968

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CHARACTERIZATION OF POLYMERS BY SOFTENING BEHAVIOR, THERMOGRAVIMETRIC ANALYSIS, AND DIFFERENTIAL THERMAL ANALYSIS

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, for which Dr. G. F. L. Ehlers is project engineer.

The manuscript was released by the authors in September, 1967 for publication as an Air Force Materials Laboratory Technical Report. It covers work conducted intermittently since 1963, with its major part between October 1966 and September 1967.

This technical report has been reviewed and is approved.

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ABSTRACT

The thermal behavior of a large number of experimental polymers has been studied. A compilation of the softening under load, thermogravimetric analysis, and differential thermal analysis has been used to determine glass transition temperatures, melting points, secondary reactions, and decomposition temperatures.

Softening under load produces a penetration versus temperature curve outlining the range in which glass transitions and crystalline melting occur. A second penetration step may indicate reactions with loss of material; an expansion often occurs, on the other hand, when formation of gases is involved. The TGA record of weight loss versus temperature is straightforward and indicative of decomposition or other reactions involving loss of material. DTA measurements required repeated runs with up to three different instruments, and rigidly controlled test conditions to obtain reproducible results and to ascertain the significance of certain transitions and eliminate those not inherent in the polymer itself. The influence of variables in DTA and the validity of test results are discussed.

On each of the polymers it is shown how the correlation of the three test results permits the determination of reversible and irreversible transitions. In a number of polymers, secondary reactions were found to occur, such as the completion of polymerization of fluorovinyl groups, decarboxylation, anhydride formation, and ring closure. Water adsorbed by the polymers caused endothermic transitions in the 110° to 140°C range.

With increasing rigidity of the polymer chain, TGA and softening curves become more and more diffuse, and no DTA transitions are found below the decomposition point. In a few cases of preladder polymers, in which all three techniques were used, it was possible to define decomposition temperatures with more certainty than by TGA alone.

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INTRODUCTION

Thermogravimetric analysis, differential thermal analysis, and to a lesser extent, the softening behavior under load have been used frequently for the characterization of polymers. As far as we know, however, these three methods have not been simultaneously applied in the determination of reversible and irreversible thermal properties of a broad range of polymers.

The softening behavior under load is actually a record of the penetration of a load into the sample. It may be an indication of a crystalline melting point, a glass transition, or loss of material caused by evaporation, sublimation, or decomposition. A reverse movement of the load indicates an expansion of the sample, frequently caused by gas formation during decomposition. While thermogravimetric analysis, as is well known, records the loss of material, differential thermal analysis indicates endothermic and exothermic reactions occurring in the polymer during heating, and also changes in the heat capacity of a polymer (baseline shifts). The causes can be manifold: Loss of volatiles, crystalline melting, and depolymerizations may result in an endothermic peak while crystallization, polymerization reactions, cross-linking, and oxidations cause exotherms. Baseline shifts may be indicative of glass transitions.

We expected that the joint application of these three methods would make the determination of thermal transitions less prone to error. This is the subject of the following study.

DISCUSSION

Seventy-five polymers, most of them experimental, were subjected to a softening-under-load determination, thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The polymers covered a wide range of structures, from vinyl to aromatic-heterocyclic, to double strand polymers. The purpose of this study was to see how much information about the thermal behavior of these polymers could be derived from the results of the three methods. Fifty-three of these polymers were selected for discussion in this report, most of them in detail, some in a somewhat cursory manner. Instruments, test conditions, and, in the case of DTA, the validity of the results will be discussed first.

SOFTENING BEHAVIOR

The automatic softening-range apparatus used for this study has been described elsewhere (Reference 1). Schematics of the basic instrument, the sample holder, and the complete instrumentation are shown in Figures 1-3. The equipment (without the mold for powdered samples) can also be used for the determination of the Vicat heat distortion temperature. For the test, the powdered polymer sample is tamped into the recess of the sample holder (ID, 5/16 in.) to a depth of 0.040 in. (1 mm). A load of 1000g bears upon the specimen through a 1/4 in. diameter steel disk. The sample is heated in an aluminum block at a rate of 150°C/hr. The vertical movement of the penetration rod is measured by a linear variable differential transformer and recorded on an X-Y recorder as penetration versus temperature. The tests with the present apparatus can only be performed in ambient atmosphere.

THERMOGRAVIMETRIC ANALYSIS

The instrument used for these tests was a differential transformer-type Chevenard thermo-balance. The heating rate was 150°C/hr, and a flow rate of approximately 200 ml/hr was used for the runs under nitrogen.

DIFFERENTIAL THERMAL ANALYSIS

Our first instrument was designed and built by the General Engineering Laboratory of the General Electric Company under Air Force Contract. The sample block assembly which fits into a quartz tube is shown in Figure 4. The whole unit fits into the furnace of the Aminco Thermobalance ("Thermograph") and was used in conjunction with this apparatus. Figure 5 shows the assembly in the open position, and Figure 6 the schematic of the unit with the block temperature well, the reference well, and the sample well. The metal parts of the sample block assembly are made of Inconel, the support rods and top plate of stainless steel. The thermocouples are made of 20-mil Pt and Pt-10% Rh wire. The unit was used with a Leeds and Northrup DC Microvolt Indicating Amplifier 9835B and a Varian 2-channel recorder. Block temperature and reference wells were filled with alumina. The temperature programming was done by the built-in unit of the Aminco "Thermograph" at heating rates of 3° and 9°C/min. The tests were run in air.

Our second instrument was the DuPont High Temperature (1200°C) DTA cell, used in conjunction with an F&M Model, 240M Power Proportioning Temperature Programmer, a Keithley 149 Amplifier, and a Honeywell Brown Electronik Recorder. Figure 7 shows that reference and sample cups are separated. We used our own steel cups with this instrument since the platinum cups normally supplied with this cell proved to be too soft to permit the removal of some of the strongly adhering residues. Heating rates used were 10°, 20°, and 30°C/min. The ambient atmosphere was air and the reference material was alumina.

The instrument presently in use is the DuPont DTA Standard Cell. A schematic drawing of the sample block is shown in Figure 8. The cell was used with the DuPont 900 Differential Thermal Analyzer at heating rates of 3°, 10°, 15°, 20°, and 30°C/min. A rate of 20°C/min seemed to give the best results with respect to sensitivity and resolution and was used most of the time. The runs were performed in air, in nitrogen, and in vacuum, with glass beads as reference material.

Each of the above instruments had their advantages and drawbacks. The GE cell seemed to have the highest sensitivity and best reproducibility but it was inconvenient to work with and difficult to clean. The DuPont High Temperature Cell seemed to give the best results at the higher temperature ranges. The reproducibility was good, provided the cups were aligned in exactly the same position within the quartz tube. This was often difficult to accomplish and required some experience. Resistors in series with the furnace were used to reduce the heat input and avoid a heat surge at the lower temperatures. The DuPont Standard Cell gave good sensitivity and reproducibility. We obtained the best results with the macro cups; the micro cups, about the size of melting point capillaries, were too small for some of the coarser polymers and gave irreproducible and erroneous results in these cases.

VALIDITY OF DTA DATA

Garn (Reference 2) states in his treatise "Thermoanalytical Methods of Investigation": "In the present state of the art, any use of data obtained by another observer must be done with considerable caution." He also points out that the peak temperature of a certain transition has been reported over a 100°C range for all types of apparatus and 30°-50°C routinely for the same general type. In his book, he discusses in detail the reasons for these widely scattered and even irreproducible results, especially the important influence of a large number of possible variables, most of them particular to the instrument. The most important of these variables are:

Sample: Particle Size
Packing Density

Reference Material: Kind and particle size
Packing Density

Sample Holder: Dimensions
Material
Open or covered
In same block as reference material, or free standing
If in block: internally or externally heated

Thermocouple: Location in cup
Dimensions (size)
Site of recording thermocouple (block, sample, or reference cell)
Site of controlling thermocouple (block, sample, or reference cell)

Atmosphere: Type
Static or dynamic
Flow rate
Through sample or above sample

Heating Rate

Other just as important factors are also involved, which are not listed above. There may be accidental and erroneous "transitions" resulting from shifting of material. Decomposition

reactions in most cases give a variety of irreproducible transitions caused by loss of material or loss of contact of the thermocouple with the material because of gas bubbles. A bad contact on a slide wire during our own investigations gave a highly reproducible "Baseline shift." Difficulties in interpretation are also involved. It is often very difficult to distinguish between a peak and a return to the baseline with a subsequent peak, or between a baseline shift and an endotherm or exotherm.

As far as our own results are concerned, we found that the reproducibility was quite good (within a few degrees) when the same instrument was used under exactly the same conditions. This even included running the samples the same day, making it more likely that even minor peculiarities in conditions and in handling of the sample were the same. Between different instruments and/or under slightly differing conditions, reproducibility was much lower.

To obtain reliable results, we reevaluated the samples up to 20 times, and many of the samples have been run on two or all three instruments. Only those data were used, which, to the best of our judgment, could be considered reproducible. In the discussion and in Tables I and II, the range over which the results varied is shown. This range comprises a few degrees to about 20°C in most of the cases. The very few results which scatter over a wider range are sufficiently supported by other evidence, especially from the other two methods.

DISCUSSION OF TEST RESULTS

The test results of the 53 polymers are discussed and interpreted in the order in which they are listed in Table I. The softening temperature represents, as indicated in the footnote, the highest rate of penetration, or the steepest part of the curve. If penetration occurred in several steps, the highest rate of each step is given. Minor penetrations are shown in parentheses. TGA results also represent the highest rate of weight loss of the entire run or of each step. For softening and TGA, ranges had to be given in cases where the steepest part of the curve was a straight line, and no inversion point could be determined. The onset of the weight loss is shown in brackets. The DTA exotherms and endotherms represent peak temperatures; only these could be determined with sufficient accuracy. No distinction has been made in the table between DTA runs in nitrogen, air, and vacuum. We could not detect any differences which could be attributed to the atmosphere. It seems that the only way to exclude air completely from the sample is to direct inert gas through the sample. On the other hand, a tightly packed sample may behave as if no air were present, even in an ambient air atmosphere. Then again, we found the same transition attributable to the presence of air both in runs under air and under nitrogen, which indicates that air was present in the nitrogen run.

A summary of the interpretation, in the form of a list of the observed transitions, is given in Table II. In this table, T_g and T_m are obtained from DTA transitions, often supported by the softening behavior. Data under "Other Transitions" are also based on DTA results. The transitions represent peaks or baseline shifts of the DTA curve, and inversions (highest rate) of the softening and TGA curves. Although one may argue whether the onset of a weight loss, a penetration, or a DTA transition is more important than the highest rate, or the peak, it is a fact that the onset is often difficult and, in the case of DTA, almost impossible to define. And, though some of the TGA inversions may appear too high, there are more cases where the onset of degradation is unrealistically low. (In the following, the terms "melt" or "melting" are used for the crystalline melting point only.)

1. This poly(α -hydroxymethyl-ethylacrylate) sample expanded around 200°C and showed a DTA endotherm at 201°C. It seemed to decarboxylate at this temperature to form a substituted polyallylalcohol, which melts between 225°C (soft) and 260°-263°C (DTA). The polymer begins to decompose between 331°-337°C (DTA) and 340°C (TGA).

2. The softening curves of polyvinylcarbazole showed a penetration around 200°C, and a very weak DTA transition between 214° and 225°C. We believe that both corresponded to the glass transition temperature which has been observed near 200°C (Reference 3). Shock cooling of the sample did not improve the DTA signal around 200°C, but eliminated some irreproducible transitions above 360°C. These transitions and a second inflection of the softening curve at 365°C are believed to be indicative of a crystalline melting point. A structurally comparable polymer, poly(α -vinylnaphthalene), had a T_g of 162°C (Reference 4) and a T_m of 360°C.

A strong endotherm at 475°C matches the TGA inversion point at 465°C and is indicative of decomposition.

3. A very reproducible exotherm of polydivinylbenzene between 151° and 165°C was first believed to represent further reaction of residual vinyl groups. However, an endotherm in the range as above is obtained on cooling which points to a reversible transition. We cannot explain its nature at this time. Softening seems to occur around 325°C. The polymer decomposes between 420°C (TGA) and 423°-459°C (DTA).

4. A first weight loss step of polyvinylphthalic acid had an inversion point at 170°C, ending at 200°C with a weight loss of 11%. The anhydride forms at this temperature with loss of water (calculated weight loss 9.4%). The related DTA transition is between 137° and 146°C. The polyvinylphthalic anhydride formed thusly melts between 176°-192°C (DTA) and 215°C (soft.). It decomposes between approximately 370°C (DTA) and 390°C (TGA).

5. Polyvinylenefluoride had a glass transition temperature of 98°C (DTA), which is close to the inversion point of the softening curve at 90°C. The DTA exotherm between 258° and 265°C may be explained tentatively as continuing polymerization of unreacted end groups. Decomposition occurs at 380°C (TGA), and between 383° and 423°C according to DTA.

6. Polyvinylidenefluoride had a DTA endotherm in the range of 137°-172°C and an inversion of the softening curve at 150°C. Paciorek (Reference 6) observed a DTA endotherm at 167°C. These transitions are characteristic of a crystalline melting point. On instrument 1 (GE-DTA), we repeatedly observed an exotherm at 448°-458°C, and on instrument 3 (DuPont Standard DTA Cell), we noted (visual observation) an expansion of the sample at 356°C. These figures agree very well with the onset of the TGA weight loss under nitrogen at 360°C and its highest rate at 455°C. Since the DTA runs have been performed in ambient air and since weight loss in air of this sample occurs at much lower temperatures, one may conclude that DTA results with tightly packed samples correspond more to runs in inert atmosphere than to those in air.

7. After repeated heating and cooling, the melting point of polytetrafluoroethylene became constant at 325°C. No other DTA transitions, as reported by some observers, have been found.

8. Poly- α , β , β -trifluorostyrene appeared to have a glass transition temperature of 206°C (DTA); the inversion point of the softening curve was 200°C. The inversion points at 290°C (soft) and 315°C (TGA), and the DTA endotherm at 359°C represent approximately the beginning, the halfway point, and the termination of the weight loss.

9. A Nylon-6, 10 sample had a DTA endotherm, characteristic of a crystalline melting point, at 222°-223°C. This value agrees with the literature. Decomposition occurred between 424° and 447°C (DTA).

10. Polydiallylmelamine melted between 90°C (soft) and 126°C (DTA). Both TGA in nitrogen and in air showed a two-step weight loss, probably connected with a separate breakdown of the two ring systems. Irreproducible transitions occurred in DTA above 437°C corresponding to the onset of the major weight loss step under nitrogen and the highest rate in air.

11. Polydiallylsulfone appeared to melt at 90°C. The weak, but reproducible DTA transition between 178° and 208°C may be further polymerization. Observed transitions at 280°C (soft), 300°C (TGA-nitrogen), 275°C (TGA-air), and the DTA transitions between 256°-365°C indicate decomposition. It is remarkable that two very reproducible decomposition transitions appear in DTA. They may possibly be connected with bond scission and the breakdown of the ring system.

12-14. Three polymers with a polyphenylene backbone apparently were too rigid for recognizable DTA transitions, and even TGA was inconclusive in one case (polymer 14). Irreproducible transitions, in this case above 234°C, may well indicate the onset of decomposition. In the case of polymer 13, the irreproducible transitions may be an indication of softening; some foaming was also observed at the "melting point."

15. Poly-m-phenylene oxide had a DTA endotherm or a baseline shift between 40° and 56°C. Since the material is largely amorphous, this may be indicative of the glass transition temperature. One of the runs showed a DTA decomposition exotherm at 502°C.

16. The DTA baseline shift of PPO between 216° and 242°C and the inversion of the softening curve at 205°C are indicative of the glass transition temperature. Karasz and O'Reilly (Reference 7) obtained a baseline shift at 225°C on shock cooling, and observed a melting endotherm at 317°C.

17. Two DTA endotherms of polyphenylene sulfide between 254° and 274°C and between 270° and 290°C can be correlated to the softening inversion at 255°C. Romeyn (Reference 8) found DTA transitions, believed to be melting endotherms at 267° and 281°C. Fyans (Reference 9), using a Perkin-Elmer Differential Scanning Calorimeter, showed that the first peak can be made to disappear by recrystallizing the sample at a rate of 10°C/min, and to reappear by recrystallizing isothermally. He interprets the first as premelting of poor crystallites. Average values for his transitions were 270° and 287°C. By shock cooling the melt he observed a glass transition at 97°C.

18. The polybiphenylene sulfonate melted at 169°C. The two higher "softening" temperatures at 238° and 266°C are indications of decomposition. This is confirmed by DTA which shows irreproducible transitions above 255°C, and gas evolution at 260°C.

19. The softening curve of the aromatic polyester had two major inversions at 280° and 360°C. The first may be related to the glass transition temperature; we found in one case a DTA baseline shift in this range. The second represents the crystalline melting point, as verified by the reproducible DTA endotherm between 377° and 392°C.

20-27. We expected that this group of polyxylylenes and polyxylylidenes would provide interesting information about structure-property relationships. However, the results obtained were few and disappointingly inconsistent. Polymers 21, 25, 26, 27 showed melting endotherms, confirmed by the softening curve; and, 22 and 27 have decomposition exotherms which were verified by TGA. Polymer 24 was considerably less stable in air than in nitrogen, and irreproducible transitions above 230°C can be attributed to oxidation. The exotherm at 186°-206°C could be interpreted as premelt crystallization even though no melting endotherm could be observed. Brown and Farthing (Reference 10) found that low molecular weight poly(p-xylylene) melts at about 220°C. The transitions found for polymers 21, 22, 25, and 26 have been confirmed by Romeyn (Reference 11).

28. This aromatic polyamide had a T_g between 258° and 282°C according to DTA and the softening curve.

29. The DTA exotherm of the polythiaphydrazide at between 157° and 172°C (and the "softening" at 150°C) represent the conversion to the polythiadiazole which is complete at about 320°C with 17% weight loss. The other exotherm at 285°-292°C may be the beginning of the decomposition of the polythiadiazole, with its highest rate at 485°C (TGA).

31, 32. These precursors of polysulfimides had melting points (from DTA) around 150°C. The transitions at 340°C (TGA) and above 290°C (DTA) of polymer 31 were originally believed to be linked to its cyclization to the corresponding polysulfimide. However, the mass spectrographic analysis of the volatiles proved that decomposition rather than cyclization occurs in this temperature range; no ammonia is formed, but carbon dioxide, carbon monoxide, and sulfur dioxide predominate. Polymer 32 had a three-step-TGA curve which may be reflecting the complex ring-closure process. Ring closure and/or decomposition begins at 355°-356°C (DTA).

33. This polybenzoxazole had a T_g in the range of 323° to 366°C, as indicated by DTA data. The corresponding break in the softening curve occurred between approximately 325° and 400°C, with the inversion point at 375°C. The polymer begins to decompose about that temperature (DTA exotherm at 385° to 390°C and onset of TGA weight loss in air at 370°C). Weight loss under nitrogen occurred above 460°C. Based on power factor measurements, Levine (Reference 10) found for the same structure a T_g of 435°C, which rose after postcuring to 449°C.

34. The DTA transition of this oxadiazole at 129°-138°C may have been caused by adsorbed water. We have no explanation for the endotherm between 231° and 241°C. The baseline shift at 276°-278°C seemed to represent the glass transition temperature. A similar thiazole polymer had a T_g of 265°C (Reference 12). The exotherm between 471° and 491°C indicates decomposition.

35. Softening and DTA transitions between 120° and 144°C appear to indicate a melting point in this range which would be much too low for a polybenzimidazole of this kind. However, this polymer may have been incompletely cyclized; the exotherm between 244° and 266°C may be indicative of further ring closure. In any case, the sample does not seem to be representative of this type of structure.

37. A decomposition exotherm was observed at 531°C.

38. Both endotherms of this polybenzimidazole, at 135°-137°C and between 425° and 445°C may be caused by decomposition; the polymer begins to lose weight at a very low temperature.

39. This polybenzimidazole exhibited a two-step breakdown (TGA). The first step very likely represents the evolution of hydrogen chloride, and the weight loss corresponds to the major part of the amount of hydrogen chloride which can form. In a separate trial, we observed its formation already at 215°C. The DTA endotherm between 251° and 270°C may be linked to this process and also the "softening" inversion at 270°C which represents a penetration of only 10% and is probably caused by loss of hydrogen chloride rather than melting. The other two DTA transitions at 293°-305°C and 342°-366°C are still within the first decomposition step; they cannot be further explained at this time.

40. This polybenzimidazole softens distinctly in the 360°C range, and we would interpret the DTA endotherm at 315°C as a melting point. This differs from results obtained by Petropoulos, who subjected the same sample to torsional braid analysis and obtained an inversion point of the relative viscosity versus temperature curve at 390°C which he interpreted as T_g (Reference 13). He ascribed the increasing rigidity of the sample above 450°C to crosslinking; onset of decomposition also occurred in this temperature range. The softening, TGA and DTA transitions in the 500°C range may all be attributed to decomposition.

41. A DTA baseline shift at 283°-290°C of this polybenzimidazole may be indicative of the glass transition temperature. Decomposition is indicated by a TGA inversion at 490°C and a DTA exotherm at 541°C.

42. A DTA exotherm between 163° and 200°C (softening inversion at approximately 160°C) may be caused by further ring closure. A possible glass transition or crystalline melting point around 320°C (softening) was not confirmed by DTA. The two DTA transitions, between 422° and 435°C and between 510° and 532°C, and the TGA inversion at 480°C, represent the decomposition of the polymer.

43. The polymer, a polytetrazolate, melted at 265°C and, shortly thereafter, decomposed with nitrogen evolution to form a polytriazole (expansion of softening curve at 275°C; TGA inversion at 265°C; DTA exotherm in the range of 258°-325°C). Decomposition occurred at 450°C (TGA).

44. A polytriazole, very similar to the one formed from polymer No. 43, had two DTA endotherms at 234°-253°C and at 348°-350°C. The polymer softened over a wide range, beginning above room temperature and ending above 400°C, with a sharp break around 335°C. Analysis showed that this polymer is impure and that we may have two melting points of two different species. The polymer decomposed between 450° (TGA) and 510°C (soft).

45. The polydithiazole seemed to have a glass transition temperature of 265°-272°C and decomposed, apparently in two steps, around 400°C and above 600°C (DTA exotherm at 394°-423°C).

47, 48. Both poly-s-triazinyleneimides softened between 200° and 250°C; polymer 48 seemed to have a T_g between 268° and 279°C. Both decomposed in the 400°-450°C range. A DTA exotherm of polymer 48 at 302°-335°C occurred in the range of onset of degradation and probably represents a reaction (crosslinking) involving the active hydrogen on the triazine ring.

49. This polysiloxypyhenylene melted at 55°-62°C (DTA). The DTA endotherm at 290°-293°C may be connected with the decomposition in air which begins at 280°C (TGA).

50-53. These preladder polymers had rather diffuse TGA curves. However, with one of the DTA instruments, the DuPont High Temperature Cell, reproducible decomposition transitions were obtained, which were closer to the TGA inversion in air than in nitrogen.

CONCLUSIONS

The glass transition temperatures and melting points of a variety of experimental polymers have been determined.

The decomposition temperatures for these polymers have been established using DTA peak temperatures and TGA inversion points. In general, the DTA and TGA results were in good agreement. In a number of cases, however, the DTA transitions were considerably lower than the TGA inversions. This occurred when the decomposition in air differed considerably from the decomposition in an inert atmosphere. Only the first or the major decomposition transition was reproducible in most of the cases. It can be exothermic or endothermic but we noted that the vast majority of the heterocyclic and ladder polymers had exothermic transitions. Crosslinking or oxidation reactions are generally exothermic. It is possible that these reactions predominate over depolymerization reactions and reactions with evolution of large amounts of gases which are more common among the polymers in the first half of Tables I and II. It should be pointed out that the decomposition temperatures listed in Table II do not sufficiently define the thermal stability of the polymers; thermal decomposition is a kinetic phenomenon that cannot be restricted to a given temperature. The data are, however, indicative of major breakdown reactions occurring at these temperatures under the conditions (e.g., heating rates) used.

A variety of other transitions have been observed. DTA endotherms were representative of the anhydride formation of polyvinylphthalic acid at 138°-170°C, decarboxylation of a poly-hydroxymethyl-ethylacrylate at 201°C, and an HCl abstraction of a chlorine containing poly-benzimidazole at 260°C. The following exothermic reactions have been observed: Thiadiazole ring closure from the corresponding polythiahydrazide at 168°C and triazole ring formation from a polytetraazolate at 258°-325°C. With a reasonable degree of probability, we found also exotherms indicative of fluorovinyl polymerization at 262°C (polymer 5), completion of benzimidazole ring closure between 170° and 249°C (polymer 35), and reaction of an active hydrogen on a triazine ring (polymer 48) at 321°C.

Some polymers, rerun after several months or more without redrying, showed adsorbed water as an endotherm between 110° and 140°C. This peak disappeared on vacuum-drying at 80°C. Water adsorption has been particularly observed with preladder and some heterocyclic polymers.

As one approaches the more rigid structures, such as ladder polymers, the amount of data which can be obtained by the methods described becomes almost nil. Little softening and penetration because of decomposition takes place, and the weight loss curve is usually rather diffuse. DTA transitions are seldom obtained except for an occasional decomposition peak. However, the use of all three methods may often provide useful information where one method alone may be inadequate.

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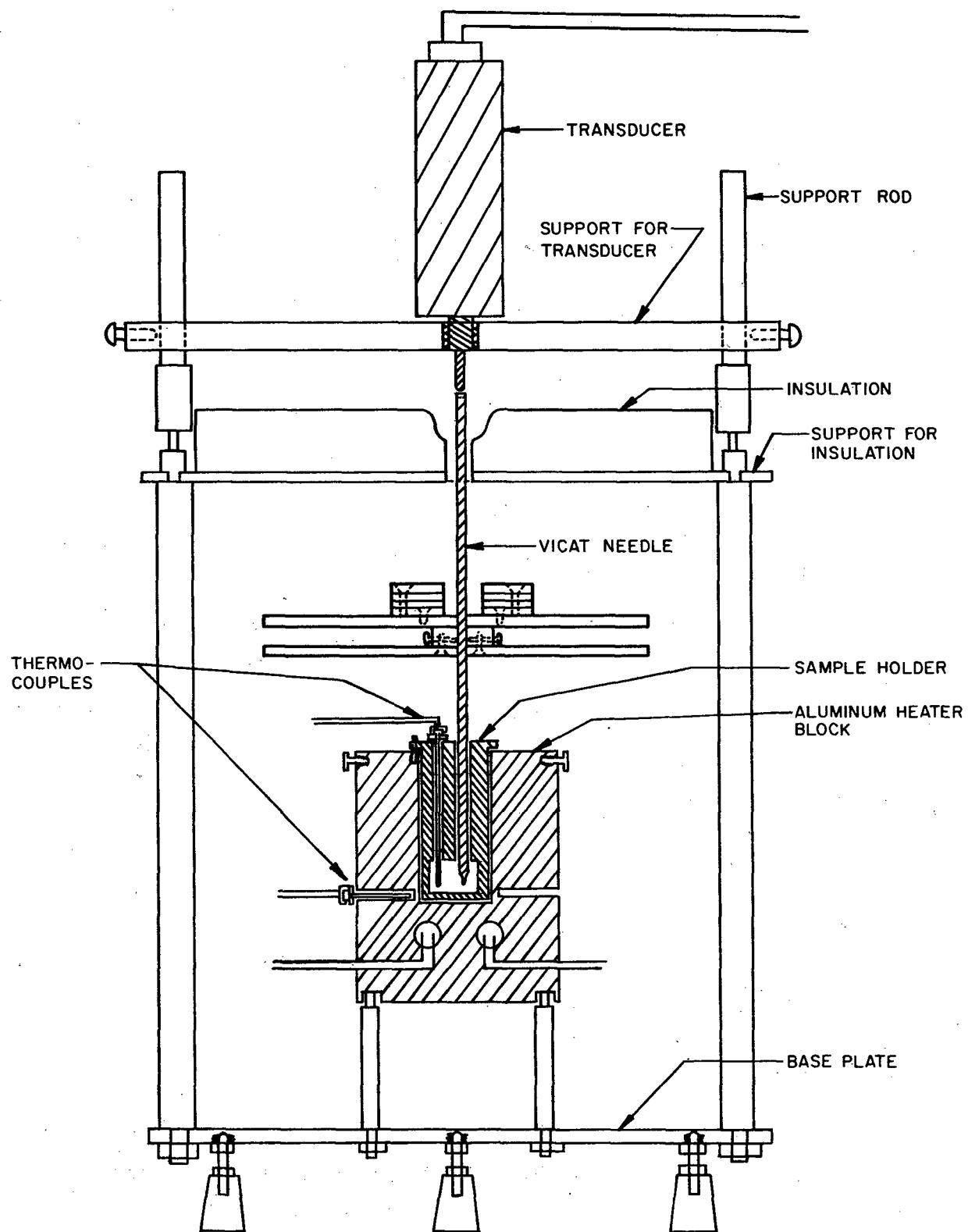


Figure 1. The Softening Range Apparatus

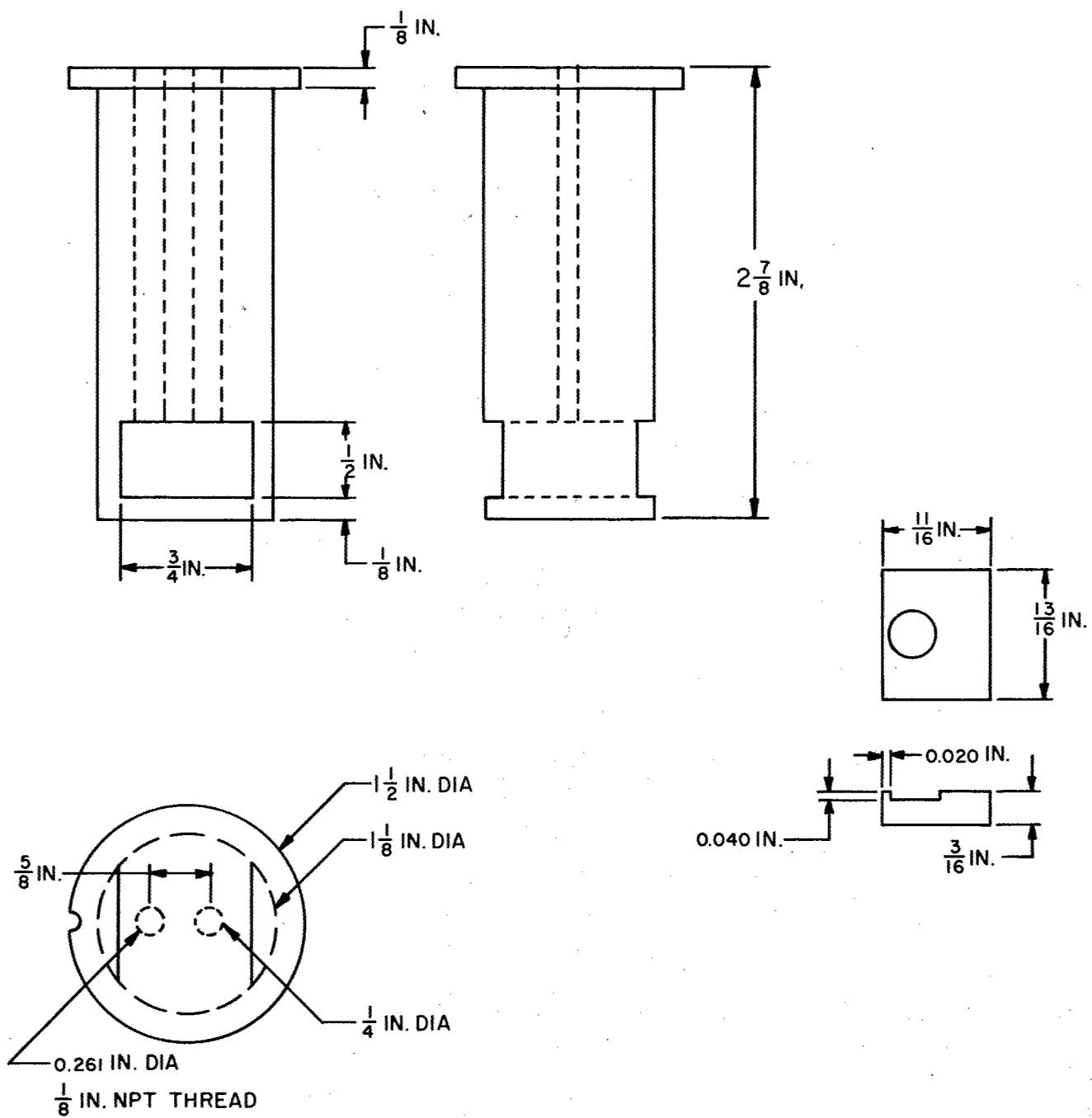


Figure 2. The Sample Holder for the Softening Range Apparatus

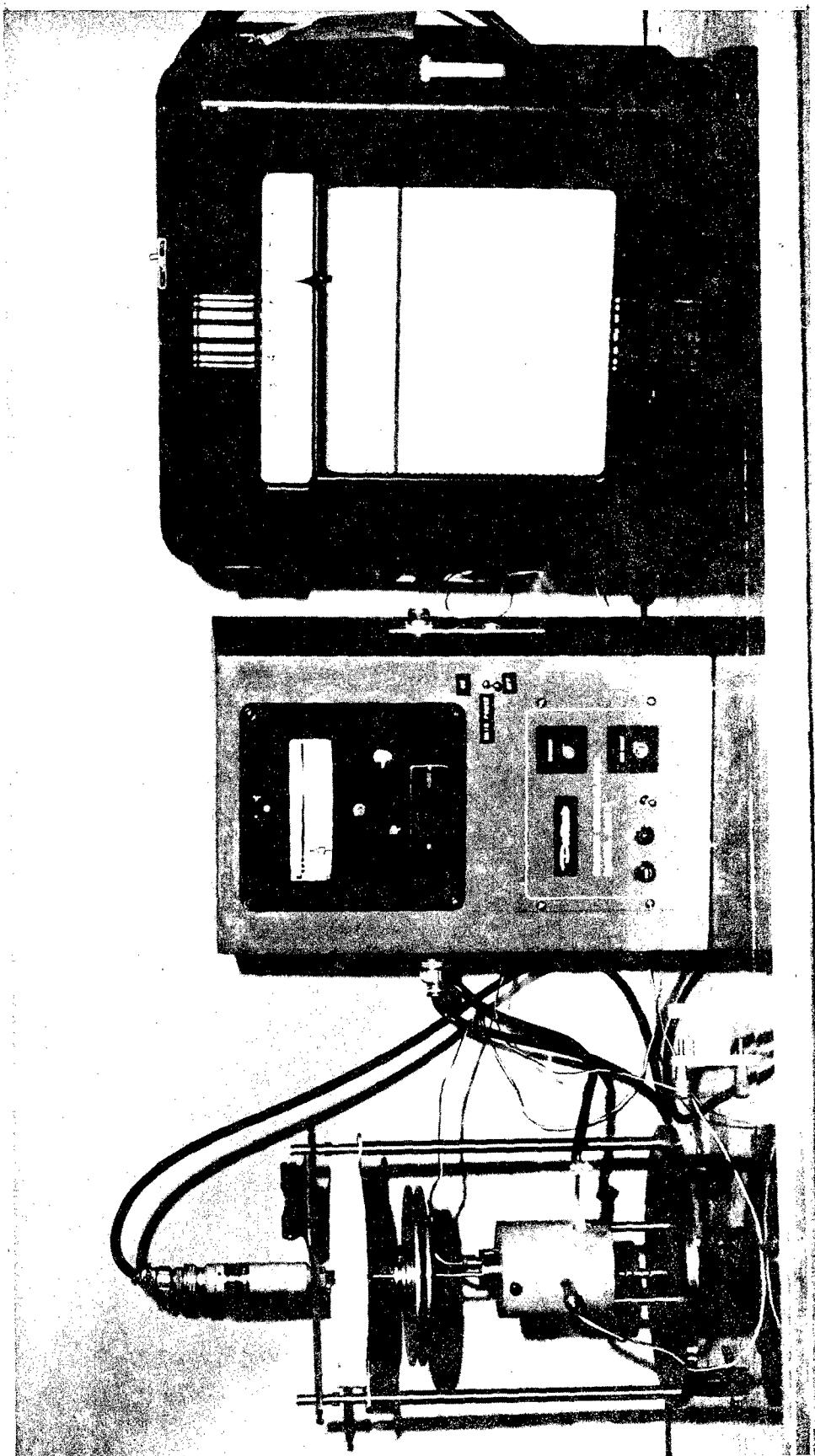


Figure 3. Automatic Softening Range Apparatus with Controller, Demodulator, and Recorder

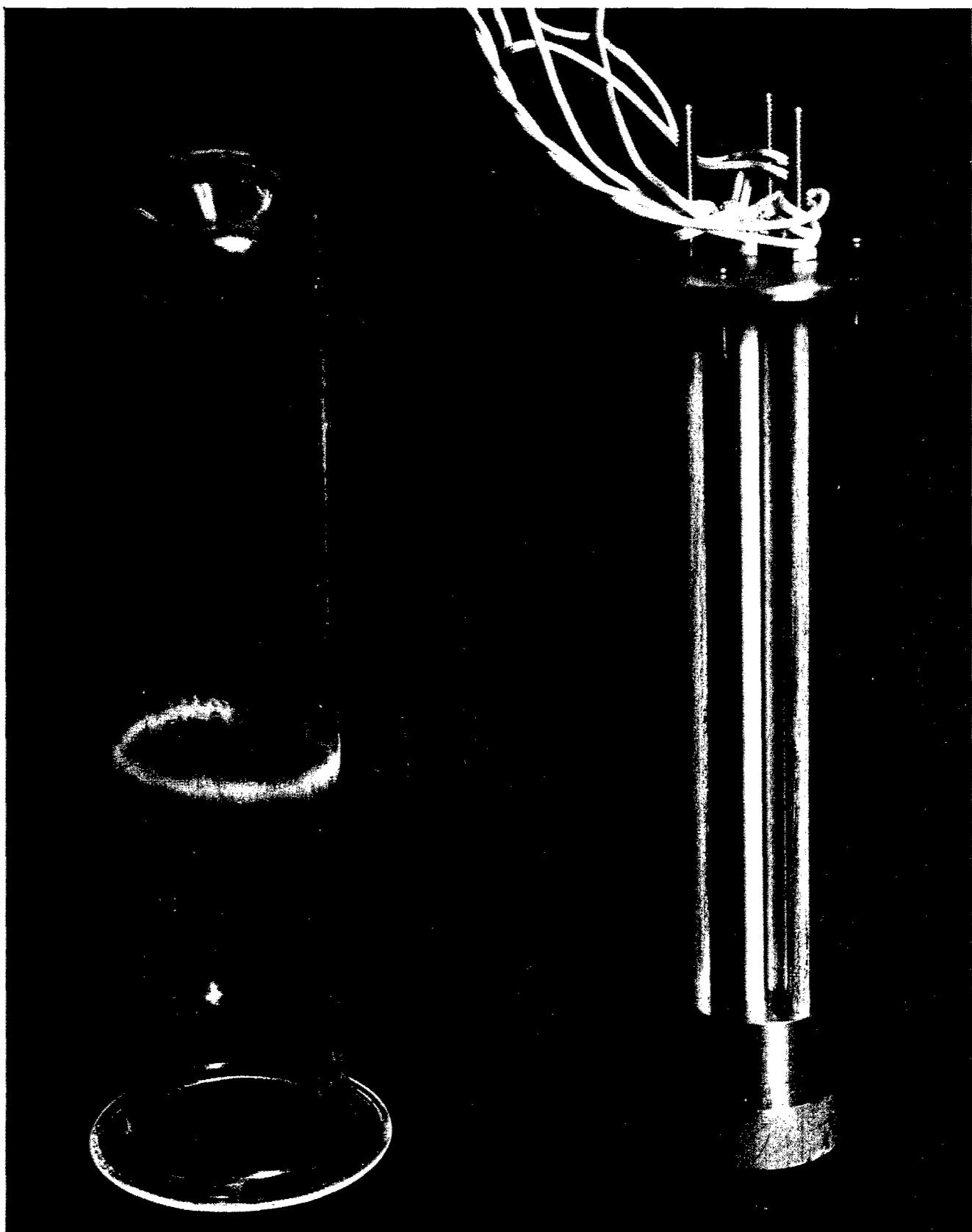


Figure 4. General Electric DTA Sample Block Assembly and Quartz Tube

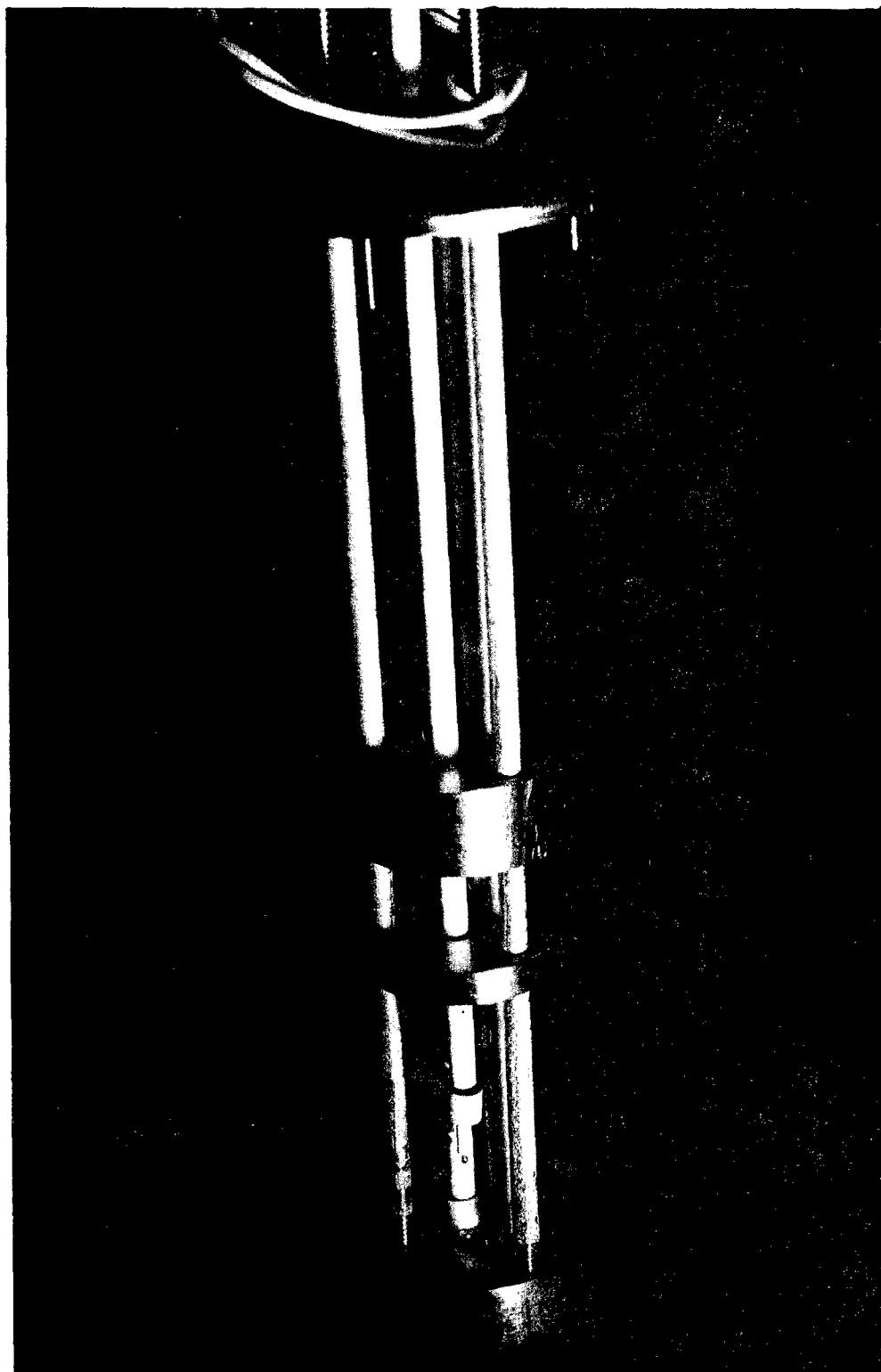


Figure 5. General Electric DTA Sample Block Assembly in the Open Position

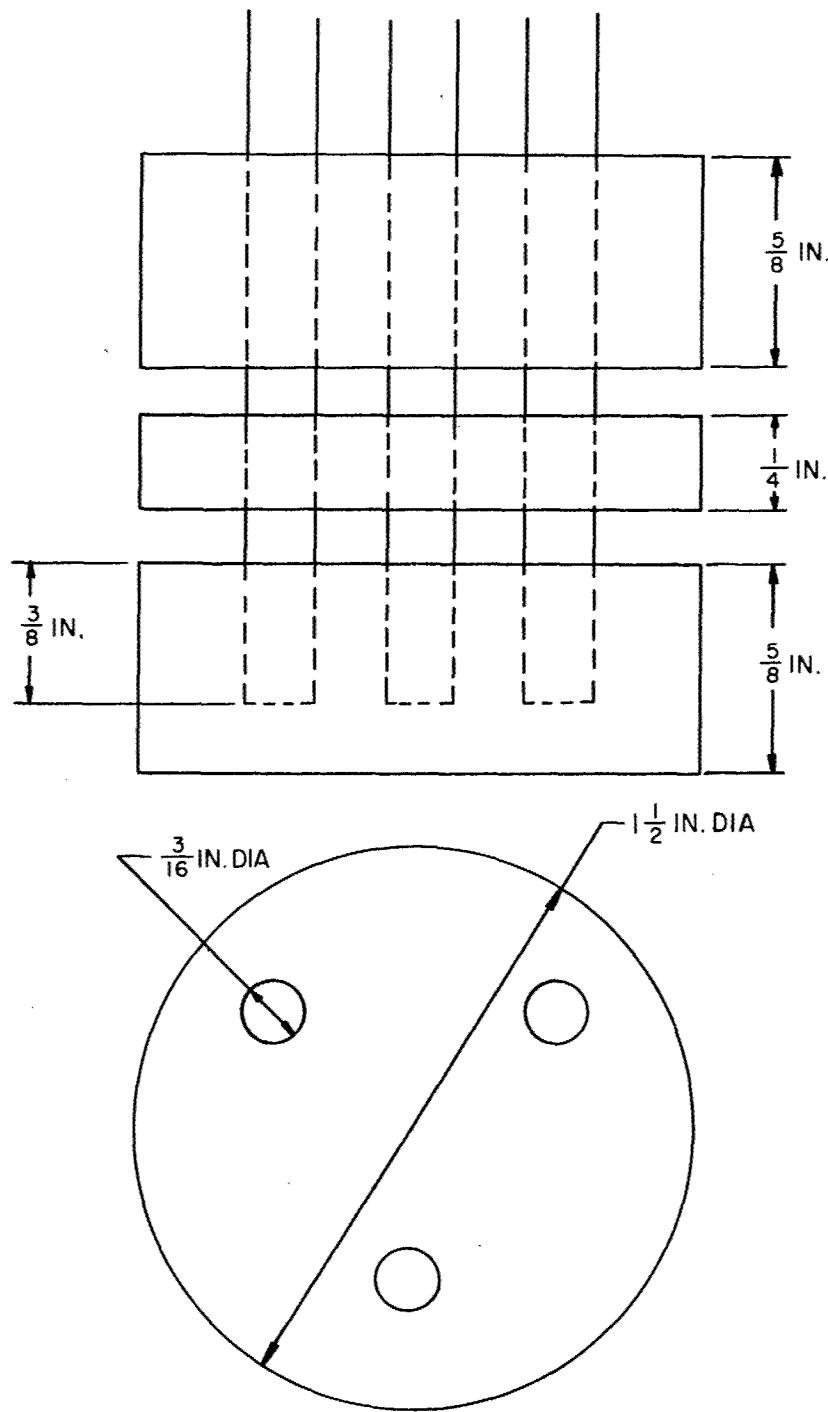


Figure 6. The General Electric DTA Sample Block Assembly

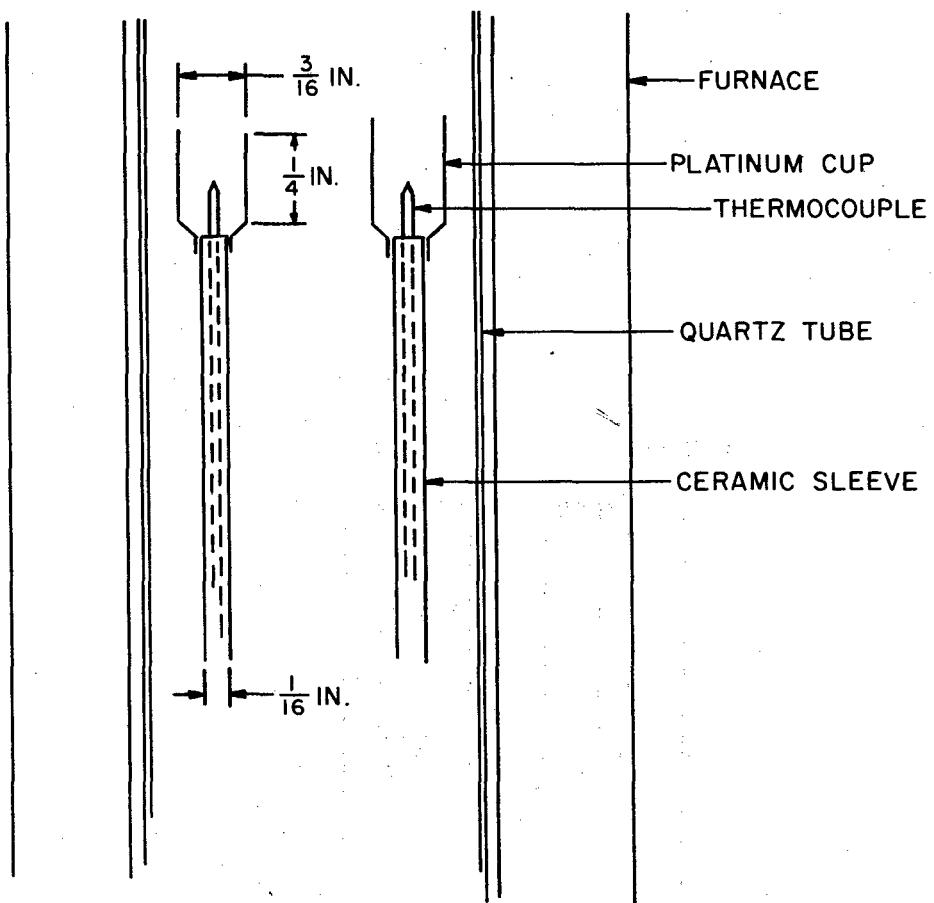


Figure 7. Part of the DuPont High Temperature DTA Cell

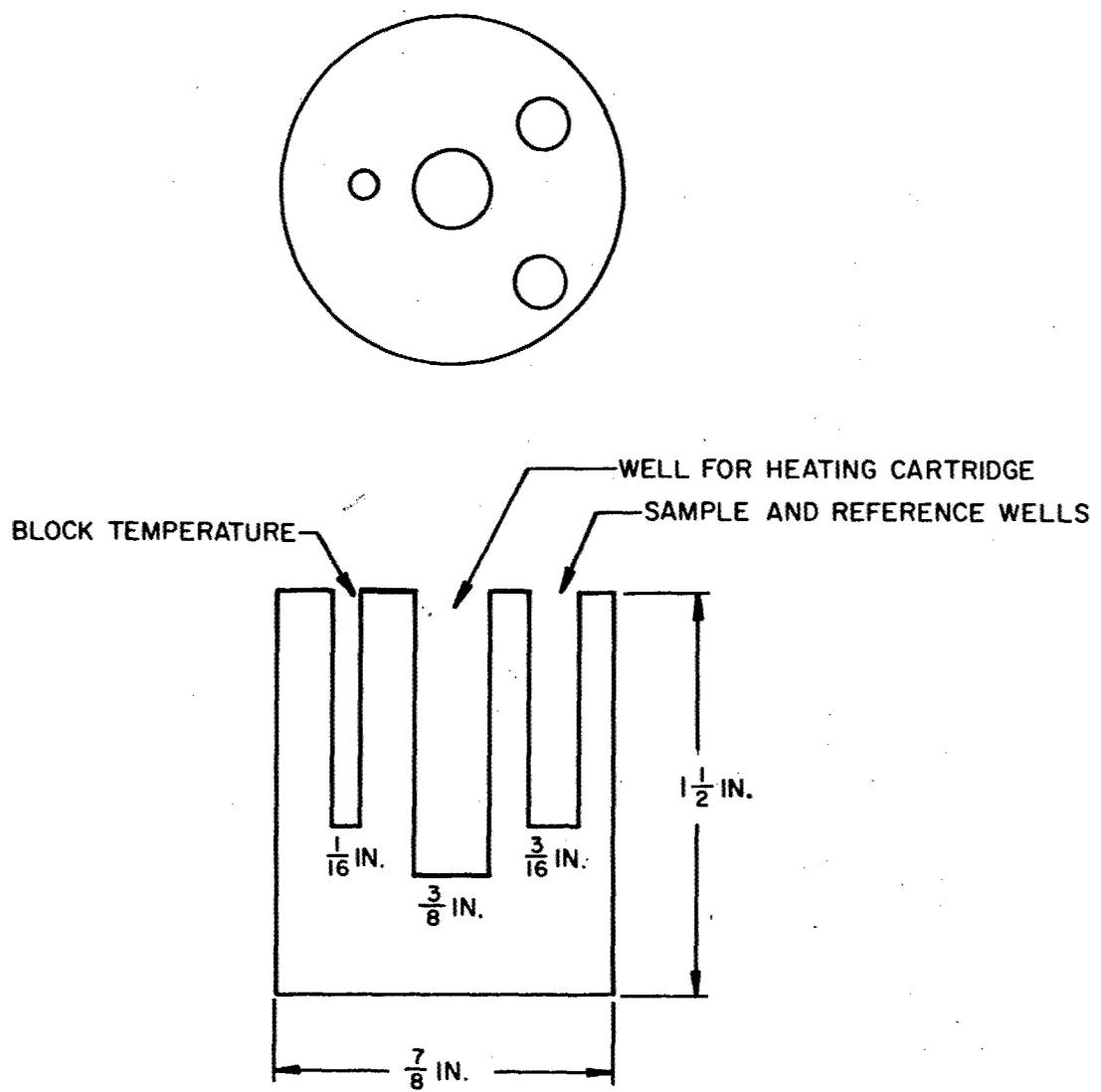


Figure 8. The Sample Block of the DuPont Standard Cell

TABLE I
TEST RESULTS

No.	Polymer Structure	Code	Source	Softening ¹⁾	TGA 2)		DTA		Total Runs	Instruments Used ⁴⁾
					Nitrogen	Air	Transitions 3)	Transitions 3)		
1	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	Koppers Co., Inc.	170; 225 Expon. at 200	[180] 340; 500	193-210 (-); 260-263 (-); 331-337 (-) 378-379 (+).		2	1		
2	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{Luvin} \end{array}$	BASF	200; 365	[375] 465	[300] 440; 485	214-225 (-w or bs); irreproduc. trans. above 360; 475 (-).		7	1, 2, 3	
3	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \\ \text{CH}-\text{C}_6\text{H}_4-\text{CH}- \\ \quad \\ \text{CH}_2-\text{CH}_2 \end{array}$	Unknown	325; 400; ~500	[330] 420	[330] 410	151-165 (+); 423-459 (-)		9	1, 2, 3	
4	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{COOH} \end{array}$	Univ. of R.I. *)	215; (330, 365)	[70; 280] 170; 390	[20, 300, 600] 175; 380; 800	137-146 (-w); 176-192 (-); irreproduc. trans. above 370.		20	1, 2, 3	
5	$-\text{CHF}-\text{CHF}-$	Peninsular Chemical Res.	90	[320] 380	--	98 (bs); 258-265 (+); 383-423 (-).		2	1, 2	
6	$-\text{CH}_2-\text{CF}_2-$	Pennsalt Chemical Corp.	(60); 150	[360] 455	[230] 295	137-172 (-); 448-458 (+) (instr. 1 only); expand. of matl. observed at 336° (instr. 3)		14	1, 2, 3	
7	$-\text{CF}_2-\text{CF}_2-$	DuPont Co.	--	[470] 570	[470] 570	337 (-); 326 (-); 325 (-) obtained on repeated heating and cooling of the same sample.				
8	$-\text{CF}_2-\text{CF}-$	Koppers Co., Inc. *)	200; 290	[225] 315	[290] 320-340	206 (bs); 359 (-).		2	1	
9	$-\text{CO}(\text{CH}_2)_4\text{CONH}(\text{CH}_2)_6\text{NH}-$ (NYLON 6,10)	Unknown	--	--	--	222-223 (-); 424-447 (-).		2	1	

TABLE I (CONT.)

TABLE I (CONT)

No.	Polymer Structure	Code	Source	Softening 1)	TGA 2)		Total Runs	Instruments Used 4)
					Nitrogen	Air		
19		K28R	G. E. Co.	(130); 280; 360	[400]	[375]	377-392 (-)	8 1, 2, 3
20		BEJ-XIV-195	U. S. Rubber Co. *)	400; ~440	[510]	[440]	---	6 3
21		BEJ-XIV-101	U. S. Rubber Co. *)	60	[420]	---	80-82 (-)	4 3
22		BEJ-XXV-26	U. S. Rubber Co. *)	155-195; ~225	[440]	[270]	297-316 (+)	6 3
23		BEJ-XXV-16	U. S. Rubber Co. *)	300	[300-350]	[300]	Irreproduc. trans. above ~430.	4 3
24		BEJ-XIV-44	U. S. Rubber Co. *)	115-145; ~200	[450]	[240]	186-206 (+); irreproduc. trans. above ~230.	14 2, 3
25		BEJ-XIV-157	U. S. Rubber Co. *)	140-180; 220	[265-300]	[~200]	207-222 (-)	6 3
26		BEJ-XXV-92A	U. S. Rubber Co. *)	195	[~500]	[510]	205-215 (-w).	5 3
27		DT-A-26-A	AFML/MANP	50-100 200-400	[~170]	No distinct inversion	Between 300 and 360 (+); 104-128 (-)	3 1, 3

TABLE I (CONT)

No.	Polymer Structure	Code	Source	Softening 1)	TGA 2)		Total Runs	DTA Instruments Used 4)
					Nitrogen	Air		
28		X-101	Chemstrand Co.	260	[350] ~425	--	258-282 (fs)	7 1, 2, 3
29		P2325-144	DuPont Co. *)	~150; 265	[125] 485	--	157-172 (+); 285-292 (+)	7 1, 3
30		1025-122	Koppers Co., Inc. (')	>400	[400] 515	450-750	No reproduc. trans.	8 1, 3
31		DA-44-113	Univ. of Notre Dame *)	Onset 135; 210	[260] 340	--	149-159 (-); irreg. pattern above ~290.	3 3
32		DA-43-57- (V)	Univ. of Notre Dame *)	25-150 ~450-500	[50, 275, 550] 95; 440; 550-900	--	153-157 (-); 355-356 (+).	2 3
33		RDs-1-31 (AF-R-320)	Whittaker Corp. *)	375	[460] ~590	[~370] No distinct inversion	1. run; 322; 2. run: (-); 3. run: 366 (fs); 335-390 (+)	3 1
34		45B	Univ. of Ill. *)	--	[220] ~400	[~225] No distinct inversion	129-138 (-); 231-241 (-); 276-278 (fs); 471-491 (+)	2 1
35		KJK 1-93	Whittaker Corp. *)	120	[380] ~440, ~630	--	120-144 (-w); 244-266 (+)	6 1, 3
36		AF-R-151	Whittaker Corp. *)	50; 400; ~460-500	[80; 555] ~140; ~650	[460] No distinct inversion	No reproduc. trans.	4 1, 3
37		Univ. of Ariz. *)	--	--	[525] 690	--	531 (+).	2 1

TABLE I (CONT)

No.	Polymer Structure	Code	Source	Softening ¹⁾	TGA ²⁾		DTA	
					Nitrogen	Air	Transitions ³⁾	Total Runs
38		KM-30-3	Univ. of Ariz. *)	80; > 435	[< 100] 650-750	[~ 280] No distinct inversion	135-137 (-); 425-445 (-)	4
39		RC-34	Univ. of Ariz. *)	~ 270	[150]	--	251-270 (-); 298-305 (+); 342-366 (-).	8
40		TLP-5	Univ. of Ariz. *)	360; ~ 500	[~ 460]	[~ 400] 595	315 (-); 540 (+)	2
41		TLP-9	Univ. of Ariz. *)	~ 70; > 450	[40; ~ 400]	--	283-290 (bs); 541 (+)	1
42		Chemstrand Co. *)	265; expansion at 275	~ 160; ~ 320 > 400	[~ 380]	--	163-200 (+); 422-435 (+); 510-532 (+)	2
43		Chemstrand Co. *)	265; 450	[260; ~ 300]	[260]	265; 490	258-325 (+)	2
44		Chemstrand Co. *)	335; ~ 510	[400]	[70; 350] ~ 450	234-253 (-); 348-350 (-).	7	1, 3
45		Koppers Co., Inc. *)	230	[400] ~ 520	[300] No distinct inversion	No reproduc. trans. between the 2 instr.	5	1, 3
46		Hu-5-1B	Univ. of Mich. 350	Onset ~ 100; 400; ~ 660	[245; 520] --	265-272 (bs); 394-423 (+)	12	1, 2, 3

TABLE I (CONT)

No.	Polymer Structure	Code	Source	Softening ¹⁾	TGA ²⁾		DTA	
					Nitrogen	Air	Transitions ³⁾	Total Runs
47		23643-81-35-AII	AFML/MANP	233, 360	[~350]	415; ~540	443-465 (-)	3 1, 2
48		GF35426-262	AFML/MANP	200-250	[320]	—	268-279 (bs); 302-335 (+).	5 1, 3
49		ER-4152	Koppers Co., Inc.	50, 80-100, 315-350; expand. above 350	[390]	[280]	55-62 (-); 290-293 (-).	9 1, 3
50		OP-76	Univ. of Ariz. ^{*)}	>400	[455]	[460]	513-523 (+) (instr. 2 only)	5 2, 3
51		OP-61	Univ. of Ariz. ^{*)}	~450	[~400]	—	445-447 (+) (instr. 2 only)	5 2,3
52		OP-83	Univ. of Ariz. ^{*)}	>400	[200-400]	[350]	419-420 (+) (instr. 2 only)	5 2, 3
53		OP-109b	Univ. of Ariz. ^{*)}	>320	[350]	[~300]	463-479 (+) (instr. 2 only)	5 2, 3

1) Highest rate of penetration, °C

2) Highest rate of weight loss, °C

3) Average peak values in °C; (bs) = baseline shifts (+) = exotherm; (-) = endotherm; (w) = weak

4) 1 = G. E. experimental instrument; 2) DuPont DTA High Temperature Cell; 3) = DuPont DTA Standard Cell

*) Prepared under Air Force contract.

TABLE II

TRANSITION TEMPERATURES

Polymer	T _g	T _m	Decomposition Temperatures				Other Transitions
			DTA	TGA Air	TGA Nitrogen		
1		262	331-337	340	340		201 (decarboxylation)
2	214-215	360	475	440	465		
3	(325)		446	410	420		158 (?)
4		176-192	> 370	380	390		137-146 (anhydride formation)
5	98		383-423	--	380		258-265 (cont. polymerization)
6		137-172	448-458	295	455		
7		325	--	570	570		
8	206		359	320-340	315		
9		223	424-447	--	--		
10		126	437	440	470		
11	(90)		Between 256 and 365		300		178-208 (cont. polymerization)
12		(~200)	460-507	--	~ 675		
13	(~225)		> 233	--	510		
14	145		> 234	--	Inconclusive		
15	40-56		502	560-590	555		
16	216-242		> 330	330-570	410		
17		254-274; 270-290		450-670	480		
18	(169)		> 255	270	295		
19	(280)	377-392		465	465		

TABLE II (CONT)

Polymer	T _g	T _m	Decomposition Temperatures			Other Transitions
			DTA	TGA Air	TGA Nitrogen	
20				460	515	
21		81		--	460	
22	(between 155 and 225)		297-316	500	465	
23	(300)		> 430	~ 420	475	
24	(200)		230	240-520	470	
25		207-222		~ 500	300-575	
26		205-215		~ 700	560	
27		104-128	300-360	--	Inconclusive	
28	258-282			--	~ 425	
29			285-292 1)	--	485	1) 168 (conv. to thiadiazole)
30			--	450-750	515	
31		149-159	> 290	--	340	
32		153-157	355-356 2)	--	440	2)
33	323-366		385-390	Inconclusive	~ 590	
34	276-278		471-491 481	Inconclusive	~ 400	231-241 (-)

TABLE II (CONT)

Polymer	T_g	T_m	Decomposition Temperatures			Other Transitions
			DTA	TGA Air	TGA Nitrogen	
35		120-144	--	--	~ 440	
36			Inconclusive	~ 650		
37		531	--	690		
38			425-445	Inconclusive	650-750	135-137 (begin of decomposition?)
39			251-270; 293-305; 342-366	--	~ 340; ~ 510	251-370 decomposition with HCl-evol.
40		315	540	595	510	
41	283-290	541	--	490		
42	(320)	422-435 510-532	--	480		163-200 (completion of ring closure)
43	(265)		490	450		258-325 (conversion to triazole)
44		234-253; 348-350	~ 450	475		
45	(230)		Inconclusive	~ 520		
46	265-272	394-423	--	400; ~ 660		
47	(233)	443-465	415; 540	440		
48	268-279		--	430		302-335 (reaction of active hydrogen?)

TABLE II (CONT)

Polymer	T _g	T _m	Decomposition Temperatures			Other Transitions
			DTA	TGA Air	TGA Nitrogen	
49		55-62	290-293	400-440	415	
50			513-523	500-520	~650	
51			445-447	--	~600-700	
52			419-420	460-520	500-700	
53			463-479	~510	~640	

Open spaces indicate, that no results have been obtained.

Dashes indicate that no experiments have been run.

Data in parenthesis obtained from the softening curve only.

- 1) Of polythiadiazole
- 2) May include ring closure

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13. ABSTRACT

The thermal behavior of a large number of experimental polymers has been studied. A compilation of the softening under load, thermogravimetric analysis, and differential thermal analysis has been used to determine glass transition temperatures, melting points, secondary reactions, and decomposition temperatures.

Softening under load produces a penetration versus temperature curve outlining the range in which glass transitions and crystalline melting occur. A second penetration step may indicate reactions with loss of material; an expansion often occurs, on the other hand, when formation of gases is involved. The TGA record of weight loss versus temperature is straightforward and indicative of decomposition or other reactions involving loss of material. DTA measurements required repeated runs with up to three different instruments, and rigidly controlled test conditions to obtain reproducible results and to ascertain the significance of certain transitions and eliminate those not inherent in the polymer itself. The influence of variables in DTA and the validity of test results are discussed.

On each of the polymers it is shown how the correlation of the three test results permits the determination of reversible and irreversible transitions. In a number of polymers, secondary reactions were found to occur, such as the completion of polymerization of fluorovinyl groups, decarboxylation, anhydride formation, and ring closure. Water adsorbed by the polymers caused endothermic transitions in the 110° to 140°C range.

With increasing rigidity of the polymer chain, TGA and softening curves become more and more diffuse, and no DTA transitions are found below the decomposition point.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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In a few cases of preladder polymers, in which these other techniques were used, it was possible to define decomposition temperatures with more certainty than by TGA alone.

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